A method for determination of water content in real and model porous media in equilibrium with bulk ice or gas hydrate

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ABSTRACT

A method for estimation of water content in porous media in equilibrium with bulk ice or gas hydrate is discussed. Measurements of water potential (and/or thermodynamic activity of water) were carried out on the Decagon company WP 4 device. Two types of porous media were used: the kaolinite clay and the artificial samples with known sizes of pores (controlled pore glasses - CPG). On the base of experimental determination of water potential in porous media the thermodynamic schemes are considered for: 1) unfrozen water estimation from the equilibrium “bulk ice - confined water in hydrophilic porous media” depending on temperature (for negative temperatures on Celsius); 2) nonclathrated water content from the equilibrium “bulk gas hydrate – confined water in hydrophilic porous media” depending on temperature and pressure of gas hydrate-former (methane, natural gas, etc.). The model is applied for estimations the unfrozen and nonclathrated water contents in the pore samples.

RÉSUMÉ

Un procédé pour l’estimation de la teneur en eau à l’équilibre dans un milieu poreux en contact avec de la glace ou un hydrate de gaz est discuté. Les mesures du potentiel hydrique (et/ou de l’activité thermodynamique de l’eau) ont été effectuées à l’aide d’un appareil Decagon WP 4. Deux types de milieux poreux ont été utilisés : des échantillons artificiels dont la taille des pores est connue (verre à porosité contrôlée — CPG) et de l’argile polyminérale. Sur la base de détermination expérimentale du potentiel hydrique dans des sols, les systèmes thermodynamiques sont considérés afin d’estimer: 1) l’eau non gelée à l’équilibre « volume de glace — eau confinée dans le milieu poreux hydrophile » en fonction de la température (pour des températures négatives en Celsius); 2) la teneur en eau non clathratée à l’équilibre « hydrate de gaz — eau confinée dans le milieu poreux hydrophile » en fonction de la température et de la pression des gaz produisant de l’hydrate (méthane, gaz naturel, etc.). Le modèle est appliqué afin d’estimer la teneur en eau interstitielle non gelée et non clathratée des échantillons.

1. INTRODUCTION

Water phase in porous media can exist in liquid state (capillary and film water) as well as in solid state (ice or gas hydrate). Unfrozen water in frozen soils affect on its physic-chemical and mechanic properties. In geocryology was developed various methods for determining the unfrozen water content (i.e. pore water in equilibrium with the ice) depending on the negative temperature (in centigrade) of the frozen soil (Tsytovich, 1975; Williams & Smith, 1989; Yershov, 1998). For many years researchers have attempted to develop predictive formulas for evaluating the content of unfrozen water in the frozen soils in the range of negative temperatures (Anderson & Tice,1972; Watanabe & Mizoguchi, 2002; and others). In recent years, the interest to quantitative evaluation of phase composition of moisture in frozen sediments has considerably increased (Istomin et al., 2009; Qin et al., 2009; Dall’Amico et al., 2011; Painter & Karra, 2014). This is due to development of new methods of experimental investigations of pore water and phase equilibria in frozen soils.

Pore water may also exist in hydrate-containing soils. The pore water which is in equilibrium with gas hydrate phase we named as “nonclathrated water”. The term nonclathrated water was recently introduced (Chuvilin et al., 2011; Chuvilin & Istomin, 2012) in comparison of unfrozen water. In distinguishing from unfrozen water the nonclathrated water content depends not only the type of porous media and temperature, but in the greater degree of pressure and chemical nature of hydrate-forming gas (methane, natural gas, carbon dioxide, nitrogen, etc.).

In soil physics the water potential is used for description of the pore water thermodynamic state. There are different methods to determinate the water potential in soils (Sudnitsin, 1979; Harris, 1995; Fontana, 2001; Shein, 2005). It should be noted that the method of water potential determination in porous medium is quite simple and the method was realized in serial devices. One of such devices for measuring water potential is WP4 T, developed by Decagon Devices (USA). Water potential ψ of samples is measured automatically by condensation method (by dewpoint detection) in the temperature range. The device allows to determine the value of water potential for natural soils with different particle sizes and moisture content (Cambell et al., 2007). So, the experimental determination of water potential is a promising in the study of properties of pore water in dispersed media.

The main purpose of the paper is to demonstrate how the experimental data on water potential ψ via water content in porous media (natural soils and artificial media) may be used for thermodynamic calculations of unfrozen and nonclathrated water content as a function of pressure and temperature.

In comparison with other methods the determination of unfrozen water content in frozen soils by thermodynamic calculations from experimental data of water potential has a number of advantages. For example, the possibility of unfrozen water content curve estimation in a wide range of temperatures below 0 ^{o}C with high efficiency, good accuracy and repeatability. The calculations of pore water content in equilibrium with gas hydrates (nonclathrated water) in disperse soils is another advantage of the approach under consideration.

2. EXPERIMENTAL METHOD

The measuring by WP4–T device pore water parameters are: water potential ψ (MPa) and activity of water a as a function of moisture content *W* of the soil. The device directly measure the water vapor dew point of a gas phase in equilibrium with a porous medium with a certain moisture content *W*. Then the dew point is converted to water vapor pressure p_{wpor} over the soil sample with predetermined moisture content at a given temperature. Water potential and activity of water are defined by the following relations:

$$\psi = RT\,\frac{\rho}{M}\ln\frac{p_{wpor}}{p_W}\,, \qquad a = RT\ln\frac{p_{wpor}}{p_W}\,, \tag{1}$$

where p_{wpor}– water vapor pressure above the sample (at atmospheric pressure); p_w – the vapor pressure of the bulk water phase; *R* – universal gas constant (8.314 J/mol K); T – sample temperature (K); M – the molecular weight of water (18.015 g/mol); ρ – water density (1.0 g/cm^3).

Experimental data of pore water potential are obtained on WP4-T device, also can be recounted on the difference between of chemical potentials of pore and bulk water $\Delta\mu_{w,wpor}(W,T)$, depending on the moisture content and temperature of the sample, by the relation:

$$\Delta\mu_{W,\ wpor}\left(W,T\right) = -\psi\,\frac{M}{\rho}\,. \tag{2}$$

The $\Delta\mu_{w,wpor}(W,T)$ and porous activity of water a are related:

$$\Delta\mu_{W,\ wpor}\left(W,\,T\right) = \ -RT\ln a\ . \tag{3}$$

Thus, water potential and activity of water $a = a(W,T)$ can completely determine the thermodynamics of pore water, as functions of sample moisture content *W* and temperature *T*.

Measurements of water potential of water-saturated dispersed media on the device WP4 T are carried out by the standard method (Cambell et al., 2007). The volume of using water-saturated dispersion medium is about 3-4 cm^3. After water potential measuring of initial (maximum) water-saturation the sample is stepwise dried in air. It is controlled by weighing on analytical scales with an accuracy of 0.001 g. The moisture content of the sample is determined at each stage of drying and measuring of water potential until completely dry state. Control of the moisture content of the sample is carried out both before and after the determination of water potential.

The device WP4-T is connected to PC to automate the process of obtaining values of water potential. Automatic recording of values of water potential and temperature can be set using the standard program Hyper Terminal. The measurements of water potential for all porous media are investigated at different moisture contents in the temperature range from +15 to +40 °C.

As a result, the temperature dependence of water potential vs moisture content and temperature of samples are obtained. Values ψ are recount into activity of porous water a and difference between chemical potentials $\Delta\mu_{w,wpor}(W,T)$ by equations (1) - (2).

3. THERMODYNAMICS OF CONFINED (PORE) WATER AT POROUS MEDIA

Below we shortly discussed the themodynamics of pore water in the soil or artificial porous media (in comparison with bulk water or ice) and the method for calculations of phase equilibriums of pore water with ice and gas hydrates at different pressures and temperatures (Istomin et al., 2009).

Let's chose a bulk phase of pure liquid water at atmospheric pressure *p_o* ($p_o = 0.1013$ MPa) as a standard state. So the difference between the chemical potential of pore water (via humidity of the porous media) and the chemical potential of pure bulk water at atmospheric pressure p_o and different temperatures is under consideration. At negative Celsius temperatures, which are interested for geocryology, the standard state corresponds to a metastable phase - supercooled bulk water. Supercooled water as a metastable state exists up to ~235 K. it should be noted that the available experimental data on thermodynamic and thermophysical properties of supercooled water (vapor pressure, heat capacity, etc.) is quite robust up to 245 – 250 K (Angell, 1982 & 1983), which certainly covers the range of negative Celsius temperatures normally used in geocryology. Therefore, the choosing of metastable supercooled water as standard state from a practical point of view is not restrictive.

The thermodymanic values of supercooled water in respect of ordinary (hexagonal) ice are:

$\Delta\mu^0_{w,\,i}$ - difference between the chemical potentials bulk water and bulk ice, J/mol;

$\Delta h^0_{w,\,i}$ - difference between the molar enthalpies water and ice, J/mol;

$\Delta c^0_{w,\,i}$ - difference between the molar heat capacities water and ice, J/mol K;

$\Delta V^0_{w,\,i}$ - difference between the molar volumes water and ice,cm^3/mol, as functions of temperature T (K) at pressure p_o ($p_O = 0.1013$ MPa).

Here the subscripts denote the bulk water and ice phases, respectively. Superscript (^{o}) refers to $T_O = 273.15$ K and $p_o = 0.1013$ MPa. The same values without superscript will refer to an external pressure *p* (*p* > *p₀*) due to gas phase pressure.

Under normal conditions (at $T_O = 273.15$ K and $p_O = 0.1013$ MPa):

$\Delta\mu^o_{w,\,i} = 0$ as equilibrium between bulk phases of water and ice take place;

$\Delta h^o_{w,\,i} = \Delta h^o_{w,i}(T_O)$ = 6008.0 J/mol (specific heat of the phase transition water – ice here is taken to be equal 333.5 kJ/kg and the molecular weight of water – 18.015 g/mol);

$\Delta c^o_{w,\,i} = 36.932$ J/mol K;

$\Delta V^o_{w,i} = -1.642$ cm^3/mol.

In literature the experimental data on heat capacities of hexagonal ice and supercooled water, vapor pressure of supercooled water and other properties of supercooled water and hexagonal ice are presented (Angell, 1982 & 1983; Petrenko & Whitworth, 1999; Vargaftik, 1975).

For $\Delta c^o_{w,i}(T)$ at $T \le T_O = 273.15$ K there is an empirical dependence from experimental data (Angell*, 1982)*:

$$\Delta c^o_{w,\,i} = \Delta c^o_{w,i}(T) = 36.9328 + 28.3542\cdot 10^{-6}(T - T_0)^4$$

From water vapor pressures of supercooled water p_w and ice p_i the temperature dependence of the difference between chemical potential $\Delta\mu^0_{w,\,i} = \Delta\mu^0_{w,i}(T)$ may be calculated from thermodynamic formula:

$$\Delta\mu^o_{w,\,i} = RT\ln\frac{p_w}{p_i} + 0.1013\cdot\Delta V^o_{i,w}\,.$$

From $\Delta c^o_{w,i}(T)$ and $\Delta h^o_{w,\,i}$ the value of $\Delta\mu^o_{w,\,i}(T)$ may calculate by using thermodynamic formulas. As a result we derived the approximation formula, which is recommended for practical purpose:

$$\Delta\mu^0_{w,\,i} = \Delta\mu^0_{w,i}(T) = 6008\cdot(1-\frac{T}{T_0}) - \\ -38.2\cdot\left[T\ln\frac{T}{T_0} + (T_0 - T)\right]. \qquad (4)$$

In (4) are used the $\Delta h^o_{w,\,i} = \Delta h^o_{w,i}(T_O)$=6008.0 J/mol and the average value of supercooled water heat capacity, $\Delta\bar{c}_{w,\,i} = 38.20$ J/mol K. The dependence (4) in good agree with direct measurements of water and ice saturated pressures (Angell, 1983).

The influence of external pressure *p* (up to *p = 20-25 MPa* on chemical potentials and enthalpies may be written by using the following formulas:

$$\Delta\mu_{w,\,i}(p) \approx \Delta\mu^o_{w,i} + \Delta V^o_{w,i}\cdot(p - p_0)\,,$$

$$\Delta h_{w,\,i}(p) \approx \Delta h^o_{w,i} + \Delta V^o_{w,i}\cdot(p - p_0). \qquad (5)$$

3.1. THERMODYNAMIC PROPERTIES OF PORE WATER IN POROUS MEDIUM

Let W note the humidity of soil, g/g of dry skeleton. Thermodynamic characteristics of pore water in soil in relation to balk water properties at $p_O = 0.1013$ MPa:

$\Delta\mu_{w,\,wpor}(T, W)$ – difference between the chemical potentials of bulk water and pore (confined) water at *W* and *T*, J/mol; (at $T \le 273{,}15$ K bulk water is supercooled water);

$\Delta h_{w,\ wpor}(T, W)$ – difference between the molar enthalpies of bulk and pore water, J/mol;

$\Delta c_{w,\ wpor}(T, W) \approx 0$ – difference between the molar heat capacities of pore water and bulk water, J/mol K;

$\Delta V_{w,\ wpor}(T, W) \approx 0$ – - difference between the molar volumes pore water and bulk water, cm^3/mol.

If *W* increasing, $\Delta h_{w,\ wpor}(T, W) \to 0$, but the ordinary for geocryology science assumption $\Delta h_{w,\ wpor}(T, W) = 0$ in general not fully correct.

Let's consider the equilibrium of pore water and bulk ice at $p_o = 0.1013$ MPa and $T \le T_o$:

$$\mu_{wpor}(T, W) = \mu_i^o(T) \text{ or } \Delta\mu_{w,\ wpor}(T, W) = \Delta\mu_{w,\ i}^o(T).$$

From (4):

$$\Delta\mu_{w,\ wpor}(T, W) = 6008 \cdot (1 - \frac{T}{T_o}) - -38.2 \cdot \left[T \ln \frac{T}{T_o} + (T_o - T) \right]. \qquad (6)$$

If we know the experimental value of $\Delta\mu_{w,\ wpor}(T, W)$, then from (6) it may be calculated the equilibrium humidity *W* of the soil as a function of *T* (at $T < 273.15$ K).

In terms of pore water activity a (as a function of sample moisture content) at atmospheric pressure we obtain:

$$-RT \ln a = 6008 \cdot (1 - T/T_0) - 38.2 \cdot \left[T \ln \frac{T}{T_0} + (T_0 - T) \right]. \qquad (7)$$

The equations (6), (7) make it possible to calculate the freezing point of pore water in the sample with specified moisture content, if water potential or water activity is measured (e.g., using the device WP4 T). In other words, from the equation (7) is determined the curve of unfrozen water content. Formula (7) is not quite convenient in practice. The correlation of the temperature beginning freezing (freezing shift ΔT_f) as a function of the pore water activity (in the range $1 \le a \le 0.6$) is obtained from the formula (7*):*

$$\Delta T_f = -85 \cdot a^4 + 345.93 \cdot a^3 - 578.46 \cdot a^2 + + 562.18 \cdot a + 28.501 \qquad (8)$$

The equation (8) is in a good agreement with the similar correlation for electrolyte solutions in the range of its applicability, at $a \ge 0.82$ (Tseitlin & Zaitsev, 1985).

For estimation ΔT_h - the depression (shift) of hydrate forming conditions, depending on the moisture content of the sample, may be used the correlations between ΔT_f and ΔT_h. Early, Yu. Korotaev (Korotaev et al., 1973) were proposed such correlation. Later, H. Najibi (Najibi et al., 2006) proposed more accurate formula:

$$\Delta T_h = 0.6825 \cdot \Delta T_f \ . \qquad (9)$$

The equation (9), strictly speaking, is obtained for aqueous electrolyte solutions. We analyzed of formula (9) and defined that for pore water the more precise coefficient is 0.674. Thus, the formula (9) is transformed to:

$$\Delta T_h = 0.674 \cdot \Delta T_f \ . \qquad (10)$$

Also the another correlation (between ΔT_h and $\ln a$) may be used:

$$\Delta T_h \approx 68.6 \cdot \ln a \ . \qquad (11)$$

The coefficient 68.6 in the formula (11) may slightly vary depending on the pressure of hydrate-forming gas (in our case, the methane gas is used).

4. CHARACTERISTIC OF POROUS SAMPLES

Two types of porous samples were used: natural kaolinite clay and artificial samples with known sizes of pores (controlled pore glasses - CPS from Asahi, Japan). The grain size distribution of kaolinite clay is presented in the Table 1.

Table 1. The dispersity of kaolinite clay.

Particle size distribution, %						
1 – 0.5mm	*0.5 – 0.25mm*	*0.25 – 0.1mm*	*0.1 – 0.05mm*	*0.05 – 0.01mm*	*0.01 – 0.005mm*	*<0.005mm*
0.7	0.5	0.4	2.9	19.5	11.2	64.8

The total content of silty-clay fractions in investigated sediment reaches 95.5%, while the part of clay fraction (<0.005 mm) is 64.8% (table 1). Mineral composition is presented by kaolinite (92%), quartz (6%) and muscovite (2%). The content of soluble salts in the soil is small; the total salt content (dry residue) is 0.04%. Specific active surface defined by the nitrogen adsorption method, is 12 m^2/g. The porosity of investigated kaolinite clay samples is 40-45%.

The CPG samples are another instigated porous medium. Their parameters determined by the manufacturer (Asahi, Japan) are in the Table 2.

Table 2. Parameters of glass beads and CPG samples*.

Name sample	Glass beads	CPG 100A	CPG 300A	CPG 500A
Nominal pore diameter (A)	-	100	300	500
Mean pore diameter (A)	-	119	309	495
Specific surface area (m^2/g)	2.7	295	103	56
Mean particle diameter (μm)	20	20	20	20
Total porosity (%)	42.5	84	85.5	85

*Porosity is calculated on the basis of measuring CPG' density and known density of SiO_2. Other parameters are measured by the CPG manufacturer (Asahi).

CPG sample is a silica powder that consists of 20 micron sized particles with the internal porous structure. Important feature of all studied CPGs is double porosity. They are characterized by intra-particle porosity and inter-particle porosity. The size of pores inside CPG particle is indicated in the CPG's name. For example, CPG 300A is a powder with particles (20 micron) and intra-particle pores diameter 300 Angstroms (30 nm). Total CPG porosity calculated from knowing CPG mass/volume ratio and pure silica density (2.65 g/cm^3) is estimated as 85%. For the calculation of the porosity inside grains (intra-particle porosity) of the CPG samples, we studied the sample of "glass beads" contained grains without internal porosity. The beads have the same particle size as CPG samples, but don't have internal porosity. Porosity of the "glass beads" powder was estimated as 42.5% on the basis of the same method as was used for the CPG porosity estimation. We can conclude that the total porosity of CPG is formed by empty space inside particles (part of total porosity) and empty space between particles (another part of total porosity). The calculated total porosity for all available CPG samples were almost the same with deviation about 2%.

5. RESULTS

The values of pore water activity are obtained for dispersed media with different water content, as the result of experimental determination of water potential (ψ , MPa) and calculations by formulas 2, 3. Water potential ψ , difference of chemical potentials $\Delta\mu_{w,\ wpor}$ and water activity a of kaolinite clay are presented in Table 3 and Fig. 1.

Table 3. The values of water potential, difference of chemical potentials and water activity of kaolinite clay.

W %	ψ, MPa	$\Delta\mu_{w,wwop}$, J/mol	α
0,6	-59,468	-1070,415	0,65
1,8	-34,368	-206,205	0,78
2,6	-20,682	-372,276	0,86
3,5	-10,212	-183,816	0,93
4,0	-9,315	-167,670	0,93
5,0	-6,244	-112,392	0,96
5,5	-4,477	-80,586	0,97
6,0	-3,730	-67,138	0,97
9,0	-2,955	-53,188	0,98
9,5	-2,547	-45,841	0,98
12,5	-1,592	-28,658	0,99
17,0	-0,951	-17,114	0,99
21,0	-0,548	-9,871	1,00

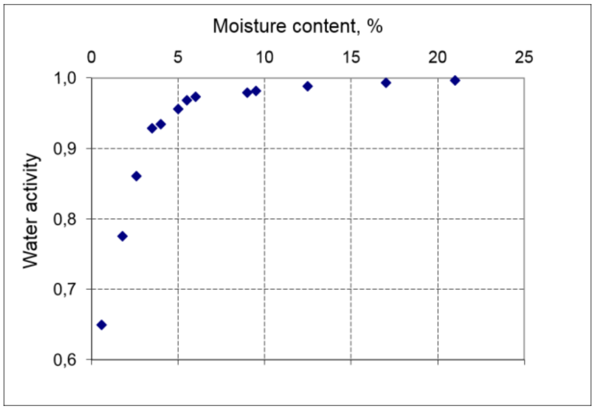

Fig. 1. Water activity values of natural kaolinite clay, depending on moisture content.

For kaolinite clay is observed every reduction of water activity values with decreasing of moisture content. Especially this trend is clearly observed at low values moisture content. The similar evenly decreasing of water activity is typical for simple artificial porous media (like glass beads) (Fig. 2). However, reducing water activity for samples CPG, unlike sample glass beads, takes place unevenly and have step. There are steps on graphs - areas where water activity value virtually unchanged within a certain interval of moisture content. The constancy of water activity is explained by filling of main capillaries within the particles CPG, which have substantially the same diameter. The water activity value on the step is also reduced by reducing the diameter of the capillary. So, the value of water potential on the step for CPG 500A is 0.96-0.97, and for the CPG 100A is 0.83-0.86. Thus, the activity value depends on the moisture content of the sample and pore space structure. Porous water fills not only capillaries within the particles at high moisture content, but it fills pore space between the particles, where humidity is slightly different from the bulk water.

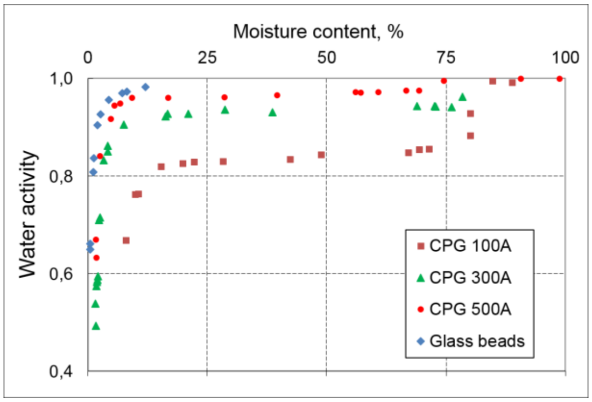

Fig. 2. Water activity values of artificial dispersed media, depending on moisture content

Difference between pore and bulk water increases with decreasing humidity. This is reflected in decreasing of its activity. A large proportion of capillary moisture with fixed size of capillaries leads in wide range of moisture its activity does not change. With a further reduction of moisture content of the sample, the capillary water will replace by the film water, which will depend on the specific surface area of the porous media and the thickness of the water film. Thus, the decreasing of moisture content is accompanied by the energy state changings of pore water, thereby reducing of its activity.

5.1. Determination of unfrozen water content

The temperature beginning freezing (freezing point) of water saturated dispersed media can be determine by using experimental water activity data and formula (6). Then proceed to the comparison of equilibrium temperature with the content of the liquid phase under these conditions. This makes it possible to determine the equilibrium water content at predetermined negative Celsius temperatures. In other words, we can calculate the quantity content of unfrozen water in a dispersion medium in a range of negative Celsius temperatures (Fig. 3). The unfrozen water content is reduced in kaolinite clay at decreasing of negative temperature of the samples. This porous media is characterized by monotonous decreasing of unfrozen water content. Fig. 3 shows the comparison of calculation results (solid line) of unfrozen water content according to your method with the experimental data (dots), obtained by the contact method. The contact method is the technique for determination of unfrozen water content is based on measuring the equilibrium water content in dried sediment plate placed in close contact with ice plate at a fixed temperature below 0 ^{o}C (Chuvilin et al., 2010 & 2011).

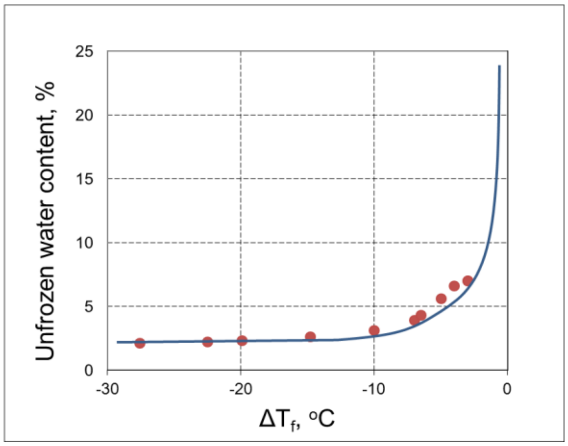

Fig. 3. Comparison of results determining of unfrozen water content for kaolinite clay, which were obtained by calculations (line) and by contact method (points).

As a result, for kaolinite clay is observed a good agreement of the experimental and calculated data (obtained by water potential) at least up to -28 °C, i.e. within a temperature range where there is freezing of main quantity of pore water. The maximum deviation between the calculated and experimental values of unfrozen water content does not exceed 0.5 %, which corresponds to the accuracy of the contact method.

The unfrozen water content is also reduced in artificial dispersed media at decreasing of negative temperature of the samples (Fig. 4).

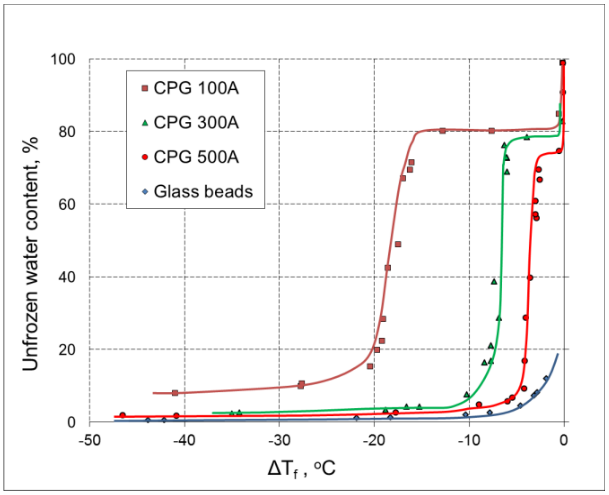

Fig. 4. Unfrozen water content in artificial dispersed media with temperature dependence.

Moreover for the sample glass beads is observed monotonous decreasing, and for the samples CPG decreasing have step. Such difference in curves is caused by different freezing temperature of water in pores between grains and within grains capillaries. The clearly dependence is traced with decreasing temperature beginning freezing of the capillary water and decreasing of capillaries size. Thus, the sample CPG 500A with capillaries of 500 A has temperature beginning freezing of -2.5 °C, and for sample CPG 100A with capillaries 100 A temperature beginning freezing it is reduced to -15 °C. Considering that in artificial samples CPG significant proportion humidity is in capillaries with specified diameter, their filling causes a sharp step change of unfrozen water content. There is only film water in porous media, when there is no capillary water. The unfrozen film water content in samples in the absence of capillary water correlates with their specific surface area (with a correlation coefficient of 0.999), despite the various negative temperatures (Table 4).

Table 4. Correlations of unfrozen film water content (W_{unf}) in artificial samples and specific surface area.

Name sample	W_{unf},%	Investigated temperature (°C)	Specific surface area (m^2/g)
Glass beads	2	-10,4	2,7
CPG 500A	2,5	-17,8	56
CPG 300A	4,1	-15,2	103
CPG 100A	9,9	-27,8	295

5.2. Determination of hydrate formation conditions and nonclathrated water content in porous media

Thermobaric methane hydrate formation conditions depending on the moisture content of the sample can be quantified from water activity data in kaolinite clay (Fig. 2) using the formula (8). Fig 5 presents conditions for methane hydrate formation in kaolinite clay.

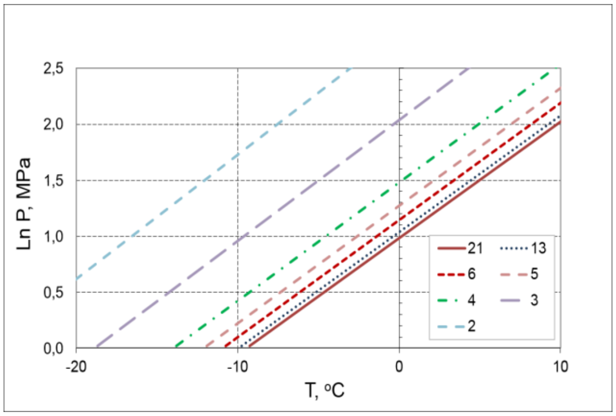

Fig. 5. Thermobaric conditions of methane hydrate formation in kaolinite clay, depending on moisture content (2, 3…21 %).

There is a displacement of hydrate formation conditions in a porous media in the direction of lower temperatures and higher pressures by reducing the moisture content of the sample, and hence with decreasing of pore water activity. The value of temperature shift ΔT_h is the most important and necessary parameter for determination of gas hydrate formation conditions in porous media. Calculations show that gas pressure in the working range (3.0 to 15.0 MPa) has no appreciable effect on the shift value ΔT_h. The analysis of experimental data allows us to trace the connection of temperature shift of hydrate formation with equilibrium moisture content (i.e. nonclathrated water) in investigated dispersed media (Fig. 6, 7).

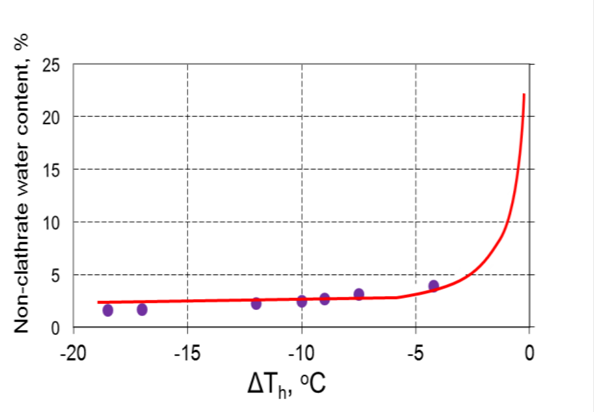

Fig. 6. Nonclathrated water content of kaolinite clay depending on the temperature shift ΔT_h, line and dots, respectively, the calculated and experimental data.

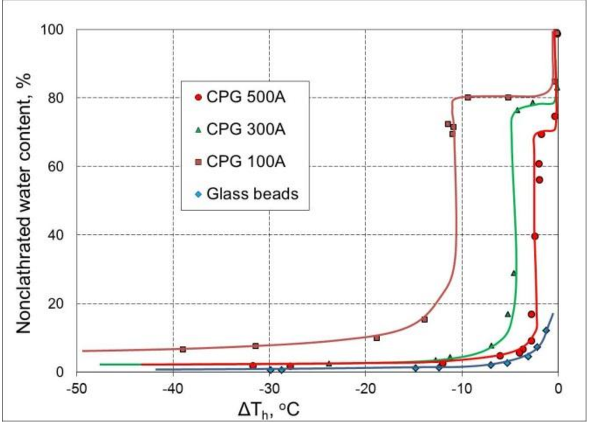

Fig. 7. Equilibrium nonclathrated water content in artificial samples depending on the temperature shift ΔT_h.

Variations of nonclathrated water content in kaolinite clay and artificial samples are similar to variations of unfrozen water content in this dispersed media. The transition of pore water into hydrate as in the case of freezing will take place in the spectrum of temperatures. The nonclathrated water content also will be determined by grain size and mineral composition of dispersed media, and their structure of pore space. The variation of nonclathrated water content in kaolinite clay and glass beads sample decreases monotonically, and in CPG samples stepwise are fixed portions of sharp reduction of nonclathrated water content, which associate with specific sizes of capillaries. The value of temperature shift relative to equilibrium temperature of the bulk water for CPG 500A is 2.4 °C, for CPG 300A is 4.6 °C, and for CPG 100A reaches 11.0 °C. In the temperature range of transition film water into hydrate, also is observed a good correlation of nonclathrated water content with specific surface area of the porous media. In Fig. 6 for kaolinite clay can note a good agreement of the calculated data of nonclathrated water content (using the water potential) with the experimental values obtained by the contact method (Chuvilin et al., 2010 & 2011). The discrepancy between the calculated and experimental data in the range of negative temperatures from -4 to -17^{o}C do not exceed 0.3%.

CONCLUSIONS

The new technique for estimation of equilibrium water content in porous media in contact with bulk ice and/or gas hydrate is discussed. The kaolinite clay and artificial samples with known sizes of pores (controlled pore glasses GPG 100, 300, 500) are used. Measurements of water potential and thermodynamic activity of water were carried out on the Decagon company WP 4 device. The thermodynamic model for description of phase equilibria “pore water – bulk ice” and “pore water – gas - gas hydrate” (for methane hydrate) is discussed. The model is applied for estimations of unfrozen and nonclathrated water contents in the pore samples like natural kaolinite clay, glass beads and CPG samples. The calculation results for the studied porous samples indicate the correlation between the content of unfrozen and/or nonclathrated water with the structure of the pore space and temperature shifts for of ice and hydrate formation. The calculated data of unfrozen and nonclathrated water contents are in a good agreement with the experimental ones obtained by the contact method.

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